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(54) PRODUCTION OF INTERLAYER FOR LAMINATED GLASS

(57)Abstract:
PURPOSE: To produce the subject interlyaer having improved transparency by irradiating a sheet made from a resin composition comprising an ethylene/vinyl acetate copolymer or an ethylene/(meth)acrylic ester copolymer and a silane coupling agent with an ionizing radiation.
CONSTITUTION: 100pts.wt. ethylene/vinyl acetate copolymer of a vinyl acetate content of 15-45wt.% or ethylene/(meth)acrylic ester copolymer of a (meth)acrylic ester content of 15-45wt.%, each of which has a melt index of 0.1-500g/10min, is mixed with 0.01-4pts.wt. silane coupling agent having at least one group selected from among amino, glycidyl and mercapto, such as 3-aminopropyltri- methoxysilane, and other additives such as an ultraviolet absorber and an antioxidant to form a resin composition. This composition is press-molded into a sheet of a thickness of 10μm to 1.6mm, and then irradiated with an ionizing radiation suck as electron beams in an atmosphere of, e.g. nitrogen at an acceleration voltage of 30 kV-2 MV at a dose of 0.5-20 Mrad to obtain the objective laminated glass interlayer of excellent transparency.

* NOTICES *

CLAIMS

[Claim(s)]
[Claim 1]Ethylene-(meta) acrylic ester copolymer 100 weight section which is an ethylene-vinylacetate copolymer or (meta) 15 to 45 % of the weight of acrylic ester content which are 15 to 45 % of the weight of vinyl acetate content, And after resin-sheet-izing a resin composition which consists of 0.01 to silane coupling agent 4 weight section which has one or more sorts of bases chosen from a group which consists of an amino group, a glycidyl group, and a sulfhydryl group, A manufacturing method of an interlayer for glass laminates irradiating with an ionizing radiation with a dose of 0.5 - 20Mrad.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention relates to the manufacturing method of the interlayer for glass laminates.
[0002]
[Description of the Prior Art]Conventionally, the interlayer for glass laminates was asked for the outstanding adhesive and tough tensile strength with glass, high transparency, etc., and the polyvinyl butyral resin plasticized with the plasticizer has been widely used for it as resin with which it is satisfied of such performances. However, above 10 **, since the autohesion nature of films was strong, the interlayer for glass laminates which consists of polyvinyl butyral resin needed to be kept at low temperature 5 ** or less, or needed to prevent blocking with the release paper, and had the fault that handling took time and effort.
[0003]The interlayer for glass laminates which consists of polyvinyl butyral resin had high hygroscopicity, and when it absorbed moisture, there was a fault that an adhesive property with glass fell. Therefore, when manufacturing a glass laminate using the interlayer for glass laminates which consists of polyvinyl butyral resin, before doubling and processing it, the humidity of an interlayer was controlled, and there was a fault that it had to be stuck by pressure under an elevated temperature and high voltage using autoclave, further, for example.
[0004]In order to solve the fault that it takes time and effort the handling of the interlayer for glass laminates which consists of the above-mentioned polyvinyl butyral resin, in JP,47-2103,B, the interlayer for glass laminates to which conversion of the ethylene-vinylacetate copolymer was carried out with acid was proposed. Since this interlayer does not have high adhesiveness in ordinary temperature, handling is easy, but. Transparency (especially haze value) was bad, and when hygroscopicity became high with the contained acid, an adhesive property with glass fell and a glass laminate was manufactured, there was a fault that it had to be stuck by pressure under an elevated temperature and high voltage.
[0005]In order to solve the fault that an adhesive property with glass falls according to moisture absorption of the interlayer for glass laminates which consists of the above-mentioned polyvinyl butyral resin, In JP,2-53381,B, the glass laminate which carries out an ethylene-vinylacetate copolymer and organic peroxide between glass plates in ** arrival, and heat-hardens was proposed.
[0006]However, since crystallinity falls at the time of a thermal denaturation, transparency of this glass laminate can improve, can keep it at ordinary temperature, can set it without gas conditioning or autoclave, and can process it, but. Since the radical generated by disassembly of organic peroxide was used for heat curing, when the working temperature of not less than 130 ** was needed and it used for the glass laminate for an ornament, the heat-resistant color needed to be used and there was a fault of bringing about aggravation of processing operation and a high cost. When it replaced with glass and a synthetic resin board was used, there was a possibility of carrying out heat modification with hot working temperature.
[0007]
[Problem(s) to be Solved by the Invention]In view of the above-mentioned fault, this invention is easy to keep at ordinary temperature, and an object of this invention is to provide the interlayer for glass laminates which can manufacture easily the glass laminate excellent in an adhesive property, shock resistance, and transparency (especially haze value).

[0008]
[Means for Solving the Problem]A resin composition used in a manufacturing method of this invention consists of an ethylene-vinylacetate copolymer or an ethylene-(meta) acrylic ester copolymer, and a silane coupling agent.
[0009]Since the shock resistance of a glass laminate which will be obtained if the transparency of a glass laminate which will be obtained if it decreases falls and increases falls, vinyl acetate content in the above-mentioned ethylene-vinylacetate copolymer is limited to 15 to 45% of the weight, and is 20 to 40 % of the weight preferably.
[0010]Acrylic ester content (meta) in the above-mentioned ethylene-(meta) acrylic ester copolymer, Since crystallinity will collapse and the tractive characteristics of a glass laminate will fall, if the transparency of a glass laminate which the processability of a glass laminate worsens since flow beginning temperature of an interlayer will rise if it decreases, and is obtained falls remarkably and increases, It is limited to 15 to 45% of the weight, and is 20 to 40 % of the weight preferably.
[0011]As for a melt index (MI) of the above-mentioned ethylene-vinylacetate copolymer or an ethylene-(meta) acrylic ester copolymer, 0.1-500g/10 minutes are preferred, and they are 0.5-400g/10 minutes more preferably.
[0012]As for the above-mentioned ethylene-vinylacetate copolymer and an ethylene-(meta) acrylic ester copolymer, a thing of the amount of polymers and a thing of low molecular weight may be used together. In that case, it is preferred that thing 0.5-20 weight-section addition of the weight average molecular weight 500-3,000 is carried out as an ethylene-vinylacetate copolymer to thing 100 weight section of the weight average molecular weight 10,000-300,000. It is preferred that thing 2-20 weight-section addition of the weight average molecular weight 500-3,000 is carried out as an ethylene-(meta) acrylic ester copolymer to thing 100 weight section of the weight average molecular weight 10,000-300,000.
[0013]The above-mentioned silane coupling agent has one or more sorts of bases chosen from a group which consists of an amino group, a glycidyl group, and a sulfhydryl group.
[0014]As the above-mentioned silane coupling agent, for example N-(2-aminoethyl)-3-aminopropyl methyl dimethoxysilane, N-(2-aminoethyl)-3-aminopropyl trimethoxysilane, 3-aminopropyldimethylmethoxysilane, 3-aminopropyl methyldiethoxysilane, 3-aminopropyl trimethoxysilane, 3-aminopropyl triethoxysilane, 3-glycidoxy propyl dimethylethoxy silane, methyldiethoxysilane (3-glycidoxy propyl), 3-glycidoxypropyltrimetoxysilane, a mercaptomethyl dimethylethoxy silane, (Mercaptomethyl) Methyldiethoxysilane, 3-mercapto propylmethyl dimethoxysilane, 3-mercapto propyltrimethoxysilane, 3-mercaptopropyl triethoxysilane, etc. are mentioned, and these may be used independently and may be used together.
[0015]Since the transparency of a glass laminate which will be obtained if the adhesive property of an interlayer and glass which will be obtained by a manufacturing method of this invention if an addition of the above-mentioned silane coupling agent decreases falls and increases falls, It is limited to 0.01 to 4 weight section to ethylene-vinylacetate copolymer or ethylene-(meta) acrylic ester copolymer 100 weight section.
[0016]Although composition of a resin composition used in a manufacturing method of this invention is as above-mentioned, a thermostabilizer, an ultraviolet ray absorbent, UV stabilizer, an antioxidant, stabilizer, etc. may be added within limits which do not spoil the physical properties of an interlayer obtained, for example.
[0017]As the above-mentioned ultraviolet ray absorbent, for example 2-(2'-hydroxy-5'-methylphenyl) benzotriazol, 2-(2'-hydroxy-5'-t-buthylphenyl) benzotriazol, 2-(2'-hydroxy-3',5'-di-t-buthylphenyl) benzotriazol, A 2-(2'-hydroxy-3'-t-butyl-5'-methylphenyl)-5-chlorobenzotriazole, A 2-(2'-hydroxy-3',5'-di-t-buthylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3',5'-di-t-amine phenyl) benzotriazol, 2 - [2'-hydroxy-3'-(3 ″4, 5, and 6″-tetrahydro phthalimidomethyl)-5'-methylphenyl] Benzotriazol systems, such as benzotriazol; 2,4-dihydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-octoxybenzophenone, 2-hydroxy-4-dodecyloxy benzophenone, 2,2'-dihydroxy-4-methoxybenzophenone, Benzophenone series;2-ethylhexyl 2-cyano 3,3'-diphenyl acrylate, such as 2,2'-dihydroxy-4,4'-dimethoxybenzophenone and 2-hydroxy-4-methoxy-5-sulfobenzophenone, Things, such as cyanoacrylate systems, such as ethyl-2-cyano 3,3'-diphenyl acrylate, are mentioned.

[0018]As the above-mentioned UV stabilizer, for example Bis(2, 2, 6, and 6-tetramethyl 4-piperidyl)

sebacate, Tetrakis (2, 2, 2, 6-tetramethyl 4-piperidyl)-1, 2 and 3, 4-butanetetracarboxylate, SanolLS-765, Sanol LS-770, Sanol LS-2626, Chimassob 944LD, Thinuvin-662, Thinuvin-662LD, Mark LA-57, Mark LA-62, and Mark. LA-63, Mark LA-67, and Mark. A hindered amine system of LA-68, Mark LA-77, Mark LA-82, Mark LA-87, and GoodriteUV-3404 grade; Nickel [2,2'-Thiobis (4-t-octyl) phenolate]-n-butylamine, Nickel dibutyl dithiocarbamate, nickel bis[o-ethyl-3,5- (di-t-butyl-4-hydroxybenzyl)] phosphate, Things, such as metallic complex systems, such as cobalt dicyclohexyl dithiophosphate and [1-phenyl, 3-methyl, 4-decano nil, and pyrazolate (5) $_2$] nickel, are mentioned.

[0019]As the above-mentioned antioxidant, for example t-butyl-hydroxytoluene (BHT), t-butyl-hydroxyanisole, 2,6-di-t-butyl-p-cresol, 2,6-di-t-butyl-4-ethylphenol, stearyl beta-(3,5-di-t-butyl-4-hydroxyphenyl) propionate, A 2,2'-methylene-screw (4-methyl-6-t-butylphenol), A 2,2'-methylene-screw (4-ethyl-6-t-butylphenol), 4,4'-thiobis(3-methyl-6-t-butylphenol), a 4,4'-butylidene-screw (3-methyl-6-t-butylphenol), 1,1,3-tris(2-methyl-4-hydroxy-5-t-buthylphenyl) butane, 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenol) butane, Tetrakis [methylene-3-(3',5'-butyl-4'-hydroxyphenyl) propionate] methane, 1,3,5-trimethyl 2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl) benzene, a screw [3,3'-bis(4'-hydroxy-3'-t-butylphenol)butyric acid] Glycol ester etc. are mentioned.

[0020]As the above-mentioned stabilizer, sodium lauryl sulfate, alkylbenzene sulfonic acid, calcium stearate soap, Zia Luca Knoll aliphatic series tertiary amine, etc. are mentioned, for example.

[0021]The above-mentioned resin composition, for example an ethylene-vinylacetate copolymer or an ethylene-(meta) acrylic ester copolymer, and a silane coupling agent, Melt kneading using a roll mill, an extrusion machine, a Banbury mixer, etc.; it is obtained by a dry blend using melt kneading machines, such as a Henschel mixer, a tumbler, and a RAIKAI machine.

[0022]In a manufacturing method of this invention, it sheet-izes with a molding method of a hot press method, the calendering roll method, extrusion sheet casting method, and an IFURESHON tube process, using the above-mentioned resin composition. It may sheet-ize by diluting and carrying out extrusion molding of the masterbatch (pellet) of an ethylene-(meta) acrylic ester copolymer which contains an additive agent in high concentration with an ethylene-(meta) acrylic ester copolymer independent pellet.

[0023]Since the shock resistance of a glass laminate which will be obtained if it becomes thin falls and the transparency of a glass laminate which will be obtained if it becomes thick falls, as for thickness of the above-mentioned resin sheet, 10 micrometers - 1.6 mm are preferred, and it is 0.1-1.2 mm more preferably.

[0024]The above-mentioned resin sheet is irradiated with an ionizing radiation in a manufacturing method of this invention. As the above-mentioned ionizing radiation, an electron beam, a gamma ray, X-rays, etc. are mentioned, and a possible electron beam has an easily preferred exposure industrially.

[0025]Various ionizing radiation accelerators, such as the Cockcroft type, a Cockcroft WARUTON type, a BANDE craft type, a high frequency type, an insulation core transformer type, a linear model, the Dynamitron type, and an electro curtain type, etc. are mentioned to an exposure of the above-mentioned ionizing radiation.

[0026]Since the mobility of an interlayer will fall and an adhesive property with glass will fall if the transparency of a glass laminate which will be obtained if it decreases falls and increases, a dose of the above-mentioned ionizing radiation is limited to 0.5 - 20Mrad, and is 1 - 15Mrad preferably. As for the above-mentioned electron beam or a gamma ray, it is preferred to glare under a high vacuum for example, under inert gas atmospheres, such as; nitrogen gas, gaseous helium, and carbon dioxide, etc.

[0027]Although accelerating voltage of the above-mentioned ionizing radiation changes with thickness of an interlayer, 30 kV - 2 MV are usually preferred, and it is 100 kV - 1,000 kV more preferably.

[0028]As a method of manufacturing a glass laminate using an interlayer obtained by a manufacturing method of this invention, For example, after putting a layered product which sandwiched an interlayer between 3-mm-thick glass plates of two sheets into the vacuum back and deaerating with a degree of vacuum of 0 - 20torr, The whole vacuum back is moved to oven, and after being stuck by pressure with a method of holding at temperature of 80-120 **, and an application-of-pressure rubber roll which had an obtained layered product heated, a method of holding at temperature of 80-120 ** in oven, etc. are mentioned.

[0029]When manufacturing the above-mentioned glass laminate, for example, it laminates with a rigid low poly membrane or papers, such as organic glass; polyester films, such as rigid body; polycarbonate other than glass, such as metal and an inorganic material, and polyurethane membrane, etc., and may be considered as a multilayer type. An ornament glass laminate can be manufactured by ornamenting at the above-mentioned rigid low poly membrane.

[0030]As lamination of an above-mentioned multilayer type glass laminate, For example, (1) Glass / interlayer / poly membrane / interlayer / glass. (2) Glass / interlayer / metal plate / interlayer / glass / poly membrane (3) glass / interlayer / paper / interlayer / organic glass / interlayer / glass (4) glass / interlayer / ornament poly membrane / interlayer / glass (5) glass / interlayer / paper / interlayer / glass is mentioned.

[0031]

[Example]Next, the example of this invention is described. That it is the following "part" means a "weight section."

(Example 1)

(1) As a manufacture ethylene-vinylacetate copolymer of a resin composition, vinyl acetate content as 100 copies of ethylene-vinylacetate copolymers ("URUTORASEN 634" by TOSOH CORP.) which are 26 % of the weight, and a silane coupling agent, As 0.5 copy of 3-aminopropyl triethoxysilane (made by Chisso Corp.), and an ultraviolet ray absorbent, As 0.3 copy of 2-(2'-hydroxy-3'-t-butyl-5'-methylphenyl)-5-chlorobenzotriazole (the "tinuvin 326" by Ciba-Geigy), and an antioxidant, 0.1 copy of t-butyl-hydroxytoluene (made by Sumitomo Chemical Co., Ltd.) was supplied to the roll mill, melt kneading was carried out at the temperature of 150 **, and the resin composition was obtained.

[0032](2) 35 copies of manufacture profitable **** resin compositions of an interlayer are fastened by two 100-micrometer-thick polyethylene terephthalate films, Press forming of the acquired fastening object was carried out for 30 minutes by 150 ** and 120 kg/cm^2 with the press-forming machine, it was neglected and the resin sheet obtained by obtaining a 400-micrometer-thick resin layer was cooled until it reached temperature of 20 **. Used the scanning electron beam irradiation device ("EPS-750" by the Nissin high voltage company) for the obtained resin sheet, carried out 6Mrad exposure of the electron beam with the accelerating voltage of 400 kV under a nitrogen atmosphere, the resin sheet was made to construct a bridge, and the interlayer was obtained.

[0033](3) To both sides of the manufacture profitable **** interlayer of a glass laminate, the float glass of a size (30 cm long, the side of 30 cm, and 3 mm in thickness) is laminated, The obtained layered product was put into the vacuum back, indirect desulfurization mind was carried out by degree-of-vacuum 10torr for 20 minutes, the vacuum bag into which the layered product went with the degassing state held was moved to oven, it held for 30 minutes at 100 **, and the glass laminate was obtained.

[0034]Only one side among the polyethylene terephthalate films which are fastening the manufacture profitable **** interlayer of the glass for adhesive strength measurement (4) Peel-off, Put the layered product obtained by laminating a 3-mm-thick float glass in the removed field into the vacuum back, and indirect desulfurization mind is carried out by degree-of-vacuum 10torr for 20 minutes, After moving to oven the vacuum bag into which the layered product went with the degassing state held and holding for 30 minutes at 100 **, it cut in 2 cm in width, and a size 10 cm in length, and the glass for adhesive strength measurement was obtained.

[0035](Examples 2-5) A glass laminate and the glass for adhesive strength measurement were obtained like Example 1 using the ethylene-vinylacetate copolymer and silane coupling agent of the specified quantity which were shown in Table 1 except having irradiated with the electron beam of the specified quantity.

[0036]As the above-mentioned ethylene-vinylacetate copolymer, in Example 2, "EVA X505" by Mitsubishi Petrochemical Co., Ltd. In Example 3, used made in Mitsui E. I. du Pont de Nemours Pori Kem Cal "EVAFLEX460", "URUTORASEN 751" by TOSOH CORP. was used in Example 4, "EVA X501" by Mitsubishi Petrochemical Co., Ltd. was used in Example 5, respectively, and the sample by Chisso Corp. was used as a silane coupling agent.

[0037](Comparative example 1) The ethylene-vinylacetate copolymer (made in Mitsui E. I. du Pont de Nemours Pori Kem Cal "EVAFLEX460") and silane coupling agent (made by Chisso Corp.) of the specified quantity which were shown in Table 1 are used, A glass laminate and the glass for adhesive strength measurement were obtained like Example 1 except not having irradiated with an electron

beam.
[0038](Comparative example 2) The silane coupling agent obtained a glass laminate and the glass for adhesive strength measurement like Example 1 using the ethylene-vinylacetate copolymer ("URUTORASEN 751" by TOSOH CORP.) of the specified quantity shown in Table 1 except not having added and not having irradiated with an electron beam.
[0039](Comparative example 3) Using the ethylene-vinylacetate copolymer ("Eve Tait 5011" by Sumitomo Chemical Co., Ltd.) of the specified quantity shown in Table 1, it did not add but the silane coupling agent obtained a glass laminate and the glass for adhesive strength measurement like Example 1 except having irradiated with the electron beam of the specified quantity.
[0040](Comparative examples 4 and 5) A glass laminate and the glass for adhesive strength measurement were obtained like Example 1 using the ethylene-vinylacetate copolymer and silane coupling agent (made by Chisso Corp.) of the specified quantity which were shown in Table 1 except having irradiated with the electron beam of the specified quantity. As an ethylene-vinylacetate copolymer, in the comparative example 4, "Eve Tait 4011" by Sumitomo Chemical Co., Ltd. was used, and "Eve Tait 5011" by Sumitomo Chemical Co., Ltd. was used by the comparative example 5, respectively.
[0041](Comparative example 6) Using the ethylene-vinylacetate copolymer ("URUTORASEN 520F" by TOSOH CORP.) of the specified quantity shown in Table 1, it did not add but the silane coupling agent obtained a glass laminate and the glass for adhesive strength measurement like Example 1 except having irradiated with the electron beam of the specified quantity.
[0042](Comparative example 7) In agitating equipment, and 5-l. three-lot a flask with a flowing-back condenser tube. 32 % of the weight of vinyl acetate content, melt-index (MI)30g/200 copies of ethylene-vinylacetate copolymers for 10 minutes ("URUTORASEN 750" by TOSOH CORP.), 300 copies of sodium hydroxide solution and 1500 copies of xylene were supplied 10% of the weight, flowing back, it stirred, the hydrolysis reaction was carried out and the partial saponification thing of 90% of the saponification degree was obtained. Supplied agitating equipment, and 5-l. three-lot a flask with a flowing-back condenser tube, and stir, 180 copies of partial saponification things, 104 copies of phthalic anhydride, 40 copies of pyridine, and 1500 copies of xylene which were obtained were made to react, flowing back at the temperature of 110 ** for 4 hours, and the resin composition was obtained. It checked ultimate analysis and that infrared-absorption-spectrum analysis was conducted and they were 3.2 % of the weight of vinyl acetate content, 16.1 % of the weight of vinyl alcohol content, 12.7 % of the weight of phthalic acid vinyl content, and 68 % of the weight of ethylene contents about the obtained resin composition. A glass laminate and the glass for adhesive strength measurement were obtained like Example 1 using the obtained resin composition except not having irradiated with an electron beam.
[0043](Comparative example 8) 25 % of the weight of vinyl acetate content, melt-index (MI)2g/100 copies of ethylene-vinylacetate copolymers for 10 minutes (made in Mitsui E. I. du Pont de Nemours Pori Kem Cal "EVAFLEX360"), Three copies of triallyl isocyanurate ("TAIKU" by Nippon Kasei Chemical Co., Ltd.), One copy of 1,1-bis(tert-butyl peroxide)-3,3,5-trimethylcyclohexane (the "par hexa 3M" by Nippon Oil & Fats Co., Ltd.) and 0.3 copy of gamma-methacryloxpropyl trimethoxy silane (made by Chisso Corp.) were supplied to the roll mill, melt kneading was carried out at the temperature of 100 **, and the resin composition was obtained. Using the obtained resin composition, the temperature in oven was 130 ** and a glass laminate and the glass for adhesive strength measurement were obtained like Example 1 except not having irradiated with an electron beam.
[0044](Comparative example 9) Although the interlayer was obtained like Example 1 using the predetermined ethylene-vinylacetate copolymer (made in Mitsui E. I. du Pont de Nemours Pori Kem Cal "EVAFLEX360") and silane coupling agent (made by Chisso Corp.) which were shown in Table 1 except having irradiated with the electron beam of the specified quantity, The obtained interlayer had the low adhesive property with glass, and a glass laminate and the glass for adhesive strength measurement were not able to be manufactured.
[0045]
[Table 1]

		エチレン－酢酸ビニル共重合体＊	シランカップリング剤		電子線照射量 (Mrad)
		酢酸ビニル含有量 (重量%)	種 類	添加量 (部)	
実施例	1	26	A	0．5	6
	2	25	B	1．0	10
	3	19	A	0．3	4
	4	28	C	0.04	3
	5	28	D	0．5	2
比較例	1	19	A	0．2	－
	2	28	－	－	－
	3	32	－	－	5
	4	20	F	0．2	0．3
	5	32	G	0．5	5
	6	8	－	－	2
	9	25	E	0.05	30

＊エチレン－酢酸ビニル共重合体１００部
A：３－アミノプロピルトリエトキシシラン
B：３－グリシドキシプロピルトリメトキシシラン
C：N－（２－アミノエチル）－３－アミノプロピルトリメトキシシラン
D：３－メルカプトプロピルトリメトキシシラン
E：３－メルカプトプロピルトリエトキシシラン
F：N－（２－アミノエチル）－３－アミノプロピルメチルジメトキシシラン
G：ビニルトリエトキシシラン

[0046]The result obtained by carrying out and evaluating a shock-proof examination and a transparency examination about the glass laminate obtained by the above-mentioned Examples 1-5 and the comparative examples 1-8 was shown in Table 2.
It carried out based on shock-proof examination JIS R3205. That is, the glass laminate held at the temperature of 23 ** and 50% of humidity for 4 hours was vertically held with the buck, and with the weight of 45 kg and an overall diameter of 75 mm ****** was dropped at the center of the glass laminate from a height of 30 cm at the pendulum type. x and the case where it did not produce were shown for the case where a ball 75 mm in diameter produces the opening which can be passed freely into a destructive portion, as O. The examination was done by n= 4.
[0047]The total light transmittance (%) and the haze value (%) at the temperature of 23 ** and 50% of humidity were measured using the "integral equation turbidity meter" by transparency examination Tokyo Denshoku Co., Ltd. The examination was done by n= 10.
[0048]The result obtained by carrying out and evaluating an adhesive examination with glass about the glass for adhesive strength measurement obtained in the above-mentioned Examples 1-5 and the comparative examples 1-8 was shown in Table 2.
Peel strength (kg/cm) was measured 90 degrees with the hauling speed for 500-mm/using the glass for adhesive strength measurement held for 4 hours at the adhesive test temperature of 23 ** with

glass, and 50% of humidity with the constant-speed tension tester ("tensilon UCE500" by a cage ene tech company). The examination was done by n= 10.

[0049]

[Table 2]

		耐衝撃性	透明性 全光線透過率 (%)	透明性 ヘイズ値 (%)	ガラスとの接着性 ピール強度 (kg/cm)
実施例	1	○	87.5	0.5	3.4
	2	○	87.3	0.4	1.9
	3	○	87.5	0.8	2.7
	4	○	88.2	0.6	1.6
	5	○	88.8	0.9	0.7
比較例	1	○	87.5	12.4	>5.0
	2	×	88.2	3.2	0.003
	3	×	89.1	0.7	0.003
	4	×	87.5	8.1	0.003
	5	×	89.1	0.7	0.04
	6	×	86.3	20.3	0.003
	7	○	86.7	1.6	0.62
	8	○	85.1	1.0	2.7

[0050](Examples 6-9) A glass laminate and the glass for adhesive strength measurement were obtained like Example 1 using the ethylene-vinylacetate copolymer and silane coupling agent of the specified quantity which were shown in Table 3 except having irradiated with the gamma ray of the specified quantity. In Example 6, as an ethylene-vinylacetate copolymer, "URUTORASEN 751" by TOSOH CORP. In Example 7, used "EVA X505" by Mitsubishi Petrochemical Co., Ltd., made in Mitsui E. I. du Pont de Nemours Pori Kem Cal "EVAFLEX460" was used in Example 8, "URUTORASEN 634" by TOSOH CORP. was used in Example 9, respectively, and the sample by Chisso Corp. was used as a silane coupling agent.

[0051](Comparative example 10) The ethylene-vinylacetate copolymer (made in Mitsui E. I. du Pont de Nemours Pori Kem Cal "EVAFLEX460") and silane coupling agent (made by Chisso Corp.) of the specified quantity which were shown in Table 3 are used, A glass laminate and the glass for adhesive strength measurement were obtained like Example 1 except not having irradiated with a gamma ray.

[0052](Comparative example 11) Using the ethylene-vinylacetate copolymer ("Eve Tait 5011" by Sumitomo Chemical Co., Ltd.) of the specified quantity shown in Table 3, it did not add but the silane coupling agent obtained a glass laminate and the glass for adhesive strength measurement like Example 1 except having irradiated with the gamma ray of the specified quantity.

[0053](Comparative example 12) A glass laminate and the glass for adhesive strength measurement were obtained like Example 1 using the ethylene-vinylacetate copolymer ("URUTORASEN 634" by TOSOH CORP.) and silane coupling agent (made by Chisso Corp.) of the specified quantity which were shown in Table 3 except having irradiated with the gamma ray of the specified quantity.

[0054](Comparative example 13) Although the interlayer was obtained like Example 1 using the ethylene-vinylacetate copolymer ("Eve Tait 4011" by Sumitomo Chemical Co., Ltd.) and silane

coupling agent (made by Chisso Corp.) of the specified quantity which were shown in Table 3 except having irradiated with the gamma ray of the specified quantity, The obtained interlayer had the low adhesive property with glass, and a glass laminate and the glass for adhesive strength measurement were not able to be manufactured.

[0055]

[Table 3]

		エチレン-酢酸ビニル共重合体* 酢酸ビニル含有量 (重量%)	シランカップリング剤 種類	シランカップリング剤 添加量 (部)	γ線照射量 (Mrad)
実施例	6	28	C	0.1	4
	7	25	A	0.2	7
	8	19	D	0.5	4
	9	26	C	0.06	3
比較例	10	19	E	0.1	−
	11	32	−	−	5
	12	26	F	0.2	0.3
	13	25	A	0.1	25

*エチレン-酢酸ビニル共重合体100部
A：3-アミノプロピルトリエトキシシラン
C：N-(2-アミノエチル)-3-アミノプロピルトリメトキシシラン
D：3-メルカプトプロピルトリメトキシシラン
E：3-メルカプトプロピルトリエトキシシラン
F：N-(2-アミノエチル)-3-アミノプロピルメチルジメトキシシラン

[0056]The result obtained by carrying out and evaluating a shock-proof examination, a transparency examination, and an adhesive examination with glass like Example 1 about the glass laminate and the glass for adhesive strength measurement which were obtained by the above-mentioned Examples 6-9 and the comparative examples 10-12 was shown in Table 4.

[0057]

[Table 4]

		耐衝撃性	透明性		ガラスとの接着性
			全光線透過率 (%)	ヘイズ値 (%)	ピール強度 (kg/cm)
実施例	6	○	88.1	0.5	3.6
	7	○	87.3	0.6	2.7
	8	○	87.5	0.8	1.9
	9	○	87.8	0.6	2.6
比較例	10	○	87.6	12.7	1.3
	11	×	89.1	0.7	0.003
	12	○	87.5	3.1	2.4

[0058](Examples 10-12, comparative examples 14-18) The ethylene-methyl methacrylate copolymer of the specified quantity shown in Table 5, a silane coupling agent, 0.3 copy of ultraviolet ray absorbent (the "tinuvin 326" by Ciba-Geigy), and an antioxidant (the Sumitomo Chemical Co., Ltd. make.) A glass laminate and the glass for adhesive strength measurement were obtained like Example 1 except having irradiated with the electron beam of the specified quantity shown in Table 5 using the resin composition which consists of the ingredient BHT. About the glass laminate and the glass for adhesive strength measurement which were obtained, the same transparency examination as Example 1 and the adhesive examination with glass were carried out and evaluated, and the result was shown in Table 5.

[0059]

[Table 5]

		エチレン-メチルメタクリレート共重合体 (100 部)	シランカップリング剤		電子線照射量 (Mrad)	全光線透過率 (%)	ヘイズ値 (%)	ガラスとの接着性
		メチルメタクリレート含有量 (重量%)	種類	添加量 (部)				ピール強度 (kg/cm)
実施例	10	25	A	0.5	6	87.2	0.7	>5.0
	11	20	B	2.0	10	86.8	0.6	2.9
	12	25	D	0.03	2	87.5	0.8	2.5
比較例	14	25	—	—	—	82.1	4.5	0.003
	15	20	—	—	—	83.0	5.6	0.002
	16	25	A	0.4	0	82.1	4.5	>5.0
	17	20	E	0.5	50	※	※	※
	18	25	A	0.2	0.2	87.5	4.0	>5.0

※：合わせガラス作製不能
A：3－アミノプロピルトリエトキシシラン
B：3－グリシドキシプロピルトリメトキシシラン
D：3－メルカプトプロピルトリメトキシシラン
E：3－メルカプトプロピルトリエトキシシラン

[0060]As for Examples 10 and 12 and the comparative examples 14, 16, and 18, "Acryft WH202" by Sumitomo Chemical Co., Ltd., Example 11, and the comparative examples 15 and 17 used "Acryft WK402" by Sumitomo Chemical Co., Ltd. as an ethylene-methyl methacrylate copolymer. The comparative examples 14 and 15 used the resin composition which consists only of an ethylene-methyl methacrylate copolymer.

[Effect of the Invention]Since the manufacturing method of the interlayer for glass laminates of this invention is as above-mentioned, an interlayer with easy handling is obtained at ordinary temperature, and it can manufacture easily the glass laminate excellent in shock resistance and transparency (especially haze value) using this interlayer. When using an ethylene-(meta) acrylic ester copolymer as the main ingredients, it can be kept at ordinary temperature and the glass laminate which doubled using this interlayer and was excellent without gas conditioning or autoclave in an adhesive property and transparency (especially haze value) at the time of processing can be manufactured easily.

[Translation done.]